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CoO$_x$ and FeO$_x$ supported on ZrO$_2$ for the simultaneous abatement of NO$_x$ and N$_2$O with C$_3$H$_6$ in the presence of O$_2$

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ABSTRACT

MeO$_x$/ZrO$_2$ (Me = Co and Fe) catalysts were studied for the simultaneous selective catalytic reduction of NO and N$_2$O in the presence of O$_2$ using C$_3$H$_6$ as reducing agent (SCR$_{sim}$). To give a better insight in the simultaneous process we investigated the reactions related to SCR$_{sim}$ (SCR$_{N2O}$, SCR$_{NO}$, N$_2$O decomposition and C$_3$H$_6$ combustion) as well as the abatements in the absence of O$_2$ (CR$_{sim}$, CR$_{N2O}$, CR$_{NO}$).

Catalytic results showed that, in the presence of O$_2$ excess, CoO$_x$/ZrO$_2$ and FeO$_x$/ZrO$_2$ catalysts were scarcely active and unselective for the separate NO and N$_2$O abatements with C$_3$H$_6$ and are ineffective for their simultaneous abatement. Because C$_3$H$_6$ preferentially reacted with O$_2$, NO was poorly reduced and N$_2$O was abated, at a temperature above that of complete C$_3$H$_6$ conversion, via both SCR$_{N2O}$ and decomposition. Conversely, in the absence of O$_2$ in the feed, on both catalysts NO and N$_2$O were efficiently reduced by C$_3$H$_6$, but undesired by-products formed.

The activity for SCR$_{sim}$ strongly depended on the C$_3$H$_6$/O$_2$ feeding ratio. With suitable feeding mixture O$_2$ was completely consumed and the residual propene efficiently and simultaneously reduced NO and N$_2$O, with negligible formation of by-products. In hydrothermal conditions both catalysts were slightly and reversibly deactivated.

Characterization by XRD, UV–vis DRS and FTIR after catalytic experiments showed that dispersed Co^{2+} and Fe^{3+} species were stable on zirconia surface and that no significant segregation phenomena occurred in hydrothermal conditions.

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1. Introduction

Nowadays a goal of environmental protection is the abatement of harmful NO$_x$ and greenhouse gases, whose emissions need to be significantly reduced. Recent focus of this approach is on N$_2$O, whose global warming potential is about 300 times higher than that of CO$_2$ and that represents 6% of the total greenhouse gas emission per year [1]. Anthropogenic N$_2$O and NO$_x$ are generated by fossil fuel combustion, industrial processes, stationary and mobile combustion sources [2]. In the exhaust gas composition of industrial (nitric and adipic acid plants) and combustion sources emitting simultaneously N$_2$O and NO$_x$, the co-existence of O$_2$, H$_2$O and CO, in amount depending on the process, should be always taken into consideration [3]. In nitric acid plants EnviNOx® process performs

the tail-gas abatement of NO$_x$ and N$_2$O over iron-containing zeolite in two catalytic beds, where NO$_x$ was abated by NH$_3$, and N$_2$O by hydrocarbons or via decomposition [4,5]. In mobile combustion sources the three-way catalytic converters (TWCs) essentially abate NO$_x$, but, depending on the operation conditions, release N$_2$O. The challenge of simultaneous abatement of N$_2$O and NO$_x$, that allows to reduce both pollutants in one catalytic bed with one reducing agent in the presence of O$_2$, is interesting to lower costs of removal strategies.

A lot of studies reviewed the separate abatement of NO$_x$ [6–9] and of N$_2$O [2,3,10–12], whereas thus far few papers addressed the attempt to abate both NO$_x$ and N$_2$O emitted from the same process in two catalytic beds [13–16] or in one catalytic bed [17–19]. Among the investigated catalysts for the process in one catalytic bed, Fe-exchanged-MFI with C3-hydrocarbons [17], Ag-ZSM5 with propene [18] and Co-MOR with CH$_4$ [19] were found active for the simultaneous abatement of NO$_x$ and N$_2$O in the presence of excess O$_2$. Because zeolite catalysts are well known to be unstable in the pres-

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ence of water vapour, leading to the active transition metal ion (tmi) segregation, ZrO_2, stable at high-temperature and able to disperse tmi at quasi-atomic level, is an alternative support. MeO_x/ZrO_2 (Me = Co or Fe) were active for the selective catalytic reduction (SCR) of NO_x with C_3H_6 [20,21] and for N_2O decomposition [22] and therefore they are possible catalysts for the simultaneous abatement. For these systems, when Me-content was below the limit up to the tmi were highly dispersed (2.0 atoms nm^{-2} for Co [20], and 2.8 atoms nm^{-2} for Fe [21]), Me^{n+} species were active sites for both SCR of NO_x [20,21] and N_2O decomposition [22]. With the aim to find a catalytic system active for the simultaneous SCR of NO_x and N_2O in the presence of excess O_2 (SCR_{sim}), and stable under real conditions, in the present paper, after explorative tests with CH_4, we studied SCR_{sim} on CoO_x/ZrO_2 and FeO_x/ZrO_2 samples with Me-content 2.2 atoms nm^{-2} using C_3H_6 as reductant. To give a better insight in the simultaneous process we investigated the reactions related to SCR_{sim} (SCR_{N2O}, SCR_{NO}, N_2O decomposition and C_3H_6 combustion) as well as the abatements in the absence of O_2 (CR_{sim}, CR_{N2O}, CR_{NO}). We also investigated the catalyst performance in hydrothermal condition (water vapor addition) and verified the stability of Me^{n+} species by XRD, UV–vis DRS and FTIR characterization after catalytic experiments.

2. Experimental

2.1. Sample preparation

The zirconia was prepared by hydrolysis of zirconium oxychloride with ammonia, as already described [23]. Before its use as a support, the material was dried at 383 K for 24 h and calcined at 823 K for 5 h. After calcination, the BET surface area of the ZrO_2 support (Z), measured by N_2 adsorption at 77 K, was 50 $m^2 g^{-1}$. XRD spectra showed that Z was in the monoclinic phase.

MeO_x/ZrO_2 catalysts (Me/Z), with Me = Co or Fe, were obtained by impregnation of Z with aqueous solution of $Co(acetate)_2$, or $Fe(nitrate)_3$ salt, drying at 383 K and calcining at 823 K for 5 h (_calcined_ samples). Co and Fe content was 2.2 atoms nm^{-2} (Atomic Absorption, Varian SpectrAA-30).

2.2. Characterization measurements

Characterization was performed on calcined samples and at the end of all catalytic measurement (_aged_ samples).

XRD measurements were done with a Philips PW 1729 diffractometer (Cu Kα, Ni-filtered radiation) equipped with an IBM computer (software APD-Philips).

The UV–vis DRS spectra were recorded in air by using a Varian Cary 5E spectrometer equipped with a computer for data acquisition and analysis (software Cary Win UV).

FTIR spectra were recorded at RT by using a Perkin Elmer Frontier spectrometer equipped with an MCT detector, collecting 64 scans at a resolution of 4 cm^{-1}. Powdered materials were pelleted (pressure 1.5×10^4 kg cm^{-2}) in self-supporting disks of ca. 50 mg cm^{-2} and 0.1-0.2 mm thickness. All samples were placed into an IR quartz cell allowing thermal treatments in vacuo or in a controlled atmosphere. Before experiments, samples were activated by heating in O_2 from RT to 773 K, keeping at this temperature for 1 h, and evacuating thereafter at the same temperature for 1 h. Spectra after adsorption of NO are difference spectra obtained by subtracting to the collected spectrum that of the blank activated sample.

2.3. Catalytic experiments

The catalytic activity was measured in a flow apparatus at atmospheric pressure. The apparatus included a feeding section where

five gas streams (He, 3% N_2O in He, 3% NO in He, 1.5% C_3H_6 in He, 10% O_2 in He) were regulated by means of independent mass flow controller-meters (MKS mod. 647C) and mixed in a glass ampoule before entering the reactor. Gas mixtures were purchased from RIVOIRA and used without further purification. The reactor was made of silica with an internal sintered frit of about 12 mm diameter supporting the powdered catalyst. Reactants and products were analysed by a gas-chromatograph (Agilent 7890A GC system), equipped with three columns (Molsieve 5A, for detecting O_2, N_2, NO and CO; Porapack Q for detecting CO_2 and N_2O; Na_2SO_4-doped alumina for detecting CH_4 and C_3H_6) and two detectors (TCD and FID). The C-balance was calculated for all experiments, whereas the N-balance only for experiments in the absence of O_2 in the feed, being NO_2 not detectable by GC-analysis. Before each run, a portion of sample (0.250 g) was heated in flow of 2% O_2/He mixture (100 $cm^3 min^{-1}$) at 773 K for 1 h. After this treatment, the reactor was by-passed and the temperature adjusted to the desired value. The reaction temperature was changed at random without intermediate activation treatment. For all reactions, the catalyst was stable as a function of the time on stream, throughout experiments lasting up to about 8 h.

The total flow rate was maintained at 50 cm^3_{STP}/min^{-1} (space velocity 24,000 h^{-1}). Conversions obtained at various (sample weight)/(flow rate) ratios (W/F) indicated that, in our conditions, reaction is under kinetic control without diffusion effect. Catalysis was run by contacting the catalyst with mixtures of various composition (v/v, He as balance): N_2O (4000 or 0 ppm), NO (4000 or 0 ppm), C_3H_6 (2000, 4000 or 0 ppm), O_2 (20000, 10000 or 0 ppm), and H_2O (10000 or 0 ppm).

Percent N_2O, C_3H_6 and O_2 conversion was calculated from (molecules-consumed)/(molecules-injected). Percent NO conversion was calculated (i) for separate abatement from $2\cdot(N_2$ produced)/(NO injected), and (ii) for simultaneous abatement from $2\cdot(N_2$ produced–N_2O converted)/(NO injected). The percent CO_2 selectivity (CO_2 rather than CO) was calculated as (CO_2 formed)/(($CO_2 + CO$) molecules-formed).

3. Results and discussion

3.1. Catalytic activity

Pure ZrO_2, that we previously found to be little active for N_2O decomposition (N_2O conversion of 32% at 773 K) [22], was inactive for the abatement of NO with CH_4 or C_3H_6 in O_2 excess, and resulted, as expected, ineffective for simultaneous abatement of NO and N_2O (data not shown).

Co/Z and Fe/Z catalysts, that we previously found to be active for N_2O decomposition [22], were inactive for SCR_{NO} with CH_4. In simultaneous abatement, SCR_{sim}, with CH_4 both catalysts abated no NO and little amount of N_2O above 723 K, being therefore ineffective (data not shown).

3.1.1. Simultaneous abatement of NO_x and N_2O with C_3H_6 in the presence of excess O_2 and related reactions (SCR_{N2O}, SCR_{NO}, N_2O decomposition, and C_3H_6 combustion).

For SCR_{sim} using C_3H_6 as reducing agent both Co/Z and Fe/Z were scarcely effective, because NO and N_2O abatements overlapped in a little temperature region (Fig. 1). In particular, NO conversion showed a volcano-shaped curve with a low maximum value, whereas N_2O conversion increased with temperature when that of NO was decreasing. On both catalysts C_3H_6 conversion (CO_2 selectivity and C-balance about 100%) markedly increased with temperature reaching 100% when N_2O abatement started. This result suggests that C_3H_6 reacted with O_2 and NO, whereas N_2O,
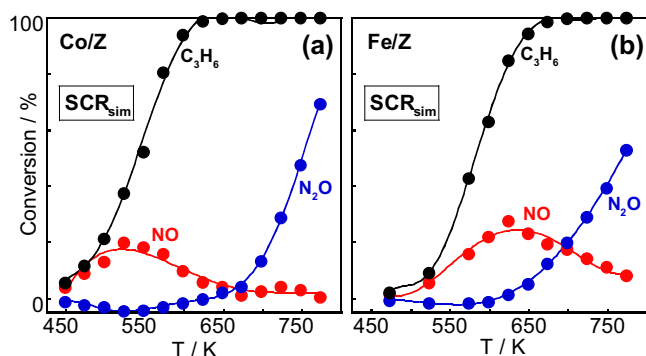
Fig. 1. SCR$_{sim}$ reaction on Co/Z (Section a) and Fe/Z (Section b): percent NO, N$_2$O and C$_3$H$_6$ conversion as a function of temperature.
Reactant mixture: N$_2$O:NO:C$_3$H$_6$:O$_2$ = 4000:4000:2000:20000 ppm (v/v).

depending on the C$_3$H$_6$ selectivity, could be reduced or decomposed.

To better investigate catalytic behaviour in the simultaneous process, we measured Co/Z and Fe/Z activity in reactions related to SCR$_{sim}$ (SCR$_{N2O}$, SCR$_{NO}$, N$_2$O decomposition, and C$_3$H$_6$ combustion) (Fig. 2).

As regards C$_3$H$_6$ consumption (Fig. 2 a and b), in combustion (CO$_2$ selectivity 100%) both systems showed high activity and Co/Z was more active than Fe/Z. In fact, combustion started and was complete at lower temperatures on Co/Z than on Fe/Z. On both catalysts propene conversion in SCR$_{N2O}$, SCR$_{NO}$ and SCR$_{sim}$ reactions was similar to that measured in combustion.

As regards NO abatement (Fig. 2c and d), both Co/Z and Fe/Z, that were completely inactive for NO decomposition, were poorly active for the SCR$_{NO}$. In agreement with previous results [20,21], in SCR$_{NO}$ C$_3$H$_6$ was mainly consumed by O$_2$ rather than NO, with a C$_3$H$_6$ selectivity (C$_3$H$_6$ consumed by NO with respect to total C$_3$H$_6$ consumed) markedly decreasing with increasing temperature. On both systems, NO conversion showed similar volcano-shaped curve in SCR$_{NO}$ and SCR$_{sim}$, suggesting that also in SCR$_{sim}$ C$_3$H$_6$ was mainly consumed by O$_2$ rather than NO. The addition of N$_2$O to the feed (SCR$_{sim}$) had no effect on NO abatement.

As regards N$_2$O abatement (Fig. 2e and f), Co/Z and Fe/Z were active in SCR$_{N2O}$. It must be considered that N$_2$O abatement occurred in a significant amount in the temperature region in which C$_3$H$_6$ was completely converted, and both catalysts were also active for N$_2$O decomposition in the presence of O$_2$ (Fig. 2e and f) and for C$_3$H$_6$ combustion (Fig. 2a and b). Because the same consideration can be made for N$_2$O abatement in SCR$_{sim}$ (Fig. 2e and f), it can be suggested that combustion competed with reduction of N$_2$O in both SCR$_{N2O}$ and SCR$_{sim}$. Taking into account that both catalysts were also active for decomposition, N$_2$O abatement could occur via reduction or via decomposition.

To assess whether the N$_2$O abatement occurred via reduction and/or via decomposition, we analysed on both samples the O$_2$ consumed/C$_3$H$_6$ consumed ratio (O$_2$/C$_3$H$_6$) in SCR$_{N2O}$ and compared it with that in combustion (Fig. 3). If the O$_2$/C$_3$H$_6$ ratio is constant as a function of temperature and equal to 4.5 (C$_3$H$_6$ + 4.5O$_2$ → 3CO$_2$ + 3H$_2$O), no reduction occurs. Because the O$_2$/C$_3$H$_6$ ratio was not constant and lower than 4.5, C$_3$H$_6$ reacted with both O$_2$ and N$_2$O. Being the stoichiometry of the reduction reaction unknown, no quantitative evaluation of C$_3$H$_6$ consumption by N$_2$O can be made and therefore the extent of N$_2$O decomposition cannot be assessed.

On the whole both systems were scarcely effective for SCR$_{sim}$ with C$_3$H$_6$, due to the competition of hydrocarbon combustion. In particular, NO was poorly abated via SCR$_{NO}$, whereas, in a different
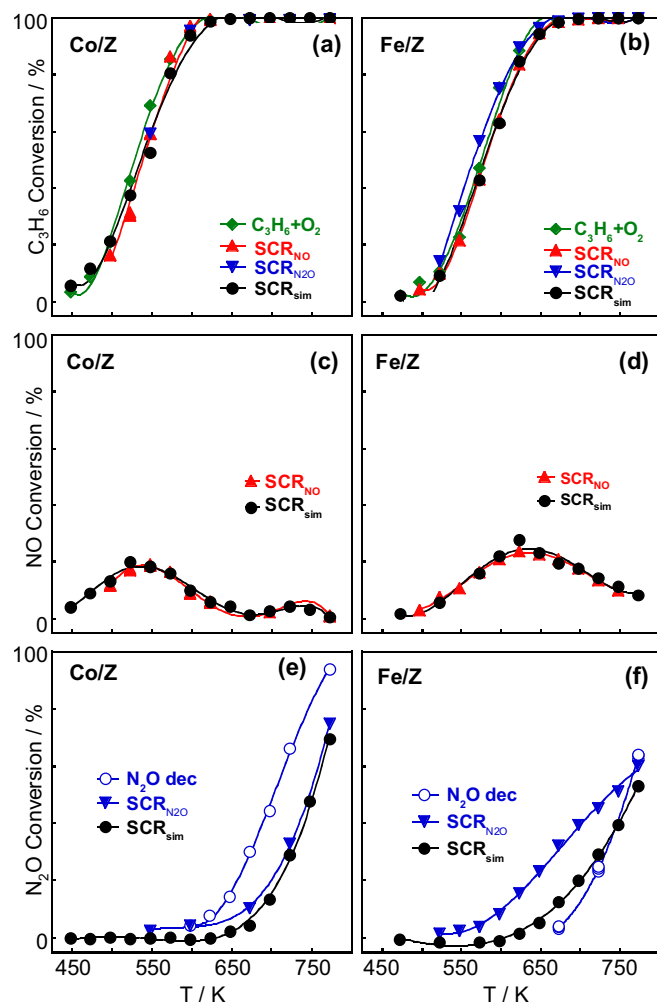
Fig. 2. Comparison between SCR$_{sim}$ and related reactions (C$_3$H$_6$ combustion, SCR$_{NO}$, SCR$_{N2O}$ and N$_2$O decomposition in the presence of O$_2$) on Co/Z (Section a, c, e) and Fe/Z (Section b, d, f). Percent C$_3$H$_6$, NO and N$_2$O conversion as a function of temperature.
Reactant mixtures: N$_2$O (4000 or 0 ppm), NO (4000 or 0 ppm), C$_3$H$_6$ (2000 or 0 ppm), O$_2$ (20000 ppm). Reactions as indicated.
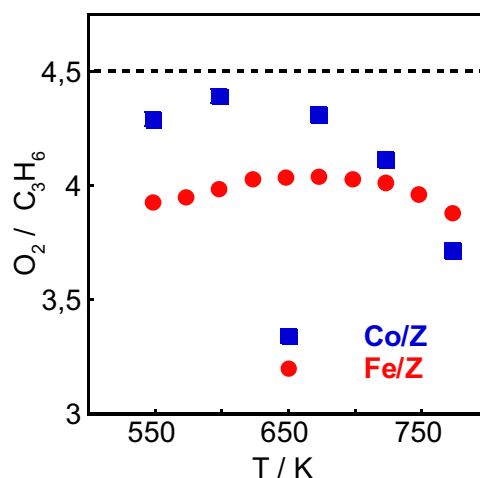
Fig. 3. O$_2$ consumed/C$_3$H$_6$ consumed ratio (O$_2$/C$_3$H$_6$) as a function of temperature for SCR$_{N2O}$ reaction on Co/Z and Fe/Z. Reactant mixture: N$_2$O:C$_3$H$_6$:O$_2$ = 4000:2000:20000 ppm (v/v).
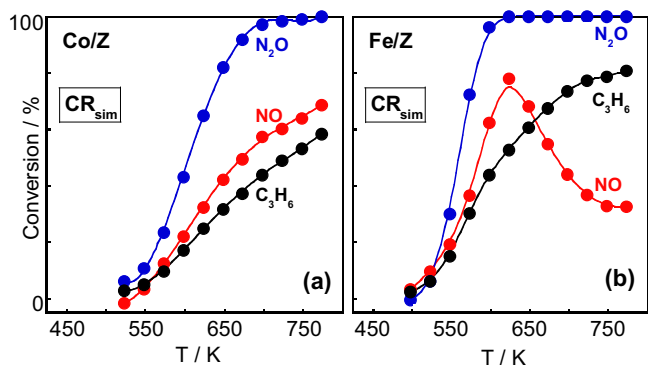
Fig. 4. CR_{sim} reaction on Co/Z (Section a) and Fe/Z (Section b): percent NO, N_2O and C_3H_6 conversion as a function of temperature. Reactant mixture: $N_2O:NO:C_3H_6 = 4000:4000:2000$ ppm (v/v).

range of temperature, N_2O was abated via reduction and possibly via decomposition.

3.1.2. Simultaneous abatement of NO and N_2O with C_3H_6 in the absence of O_2

Because propene combustion was a competitive reaction in the abatement of both NO and N_2O, we investigated on Co/Z and Fe/Z the simultaneous and separate abatements in the absence of oxygen (CR_{sim}, CR_{NO}, and CR_{N2O}).

Both catalysts, in the absence of O_2, were effective for N_2O and NO simultaneous abatement, because NO and N_2O were significantly abated in the same temperature region. NO and N_2O conversion in CR_{sim} was much higher and C_3H_6 conversion (CO_2 selectivity > 90%) lower than in the presence of O_2 (compare Fig. 4 with Fig. 1). In CR_{sim} whereas on both catalysts N_2O conversion increased with temperature up to 100%, NO conversion showed different trends. On Co/Z (Fig. 4a) the NO conversion monotonically increased and above 673 K the N-balance slightly decreased from 100 to 92%, suggesting formation of by-products. On Fe/Z (Fig. 4b) NO conversion showed a volcano-shaped curve, that above 623 K markedly decreased and by-products formed, as indicated by the parallel decrease of both C (from 100 to 91%) and N balance (from 100 to 78%). As concerns the N-balance decrease in CR_{sim}, the Nessler's reagent revealed NH_3 in the solution obtained by bubbling in water (for 60 min) the outlet mixture. Ammonia by-product possibly formed during C_3H_6 reforming in the presence of nitrogen oxides. On the contrary, in SCR_{sim} no NH_3 was revealed. As concerns the C-balance decrease, GC-FID analysis revealed small amount of C-containing by-products and the presence of a C_xN_y-containing species cannot be excluded.

In CR_{NO} both catalysts were highly active and the NO conversion curve had the same shape than that in CR_{sim} (Fig. 5). The addition of N_2O to the feed (CR_{sim}) caused a slight decrease of NO conversion.

In CR_{N2O} on both catalysts N_2O abatement occurred at a temperature much lower than that of N_2O decomposition (Fig. 5e and f) and with a N_2O consumed/C_3H_6 consumed ratio about 9 ($C_3H_6 + 9N_2O \rightarrow 3CO_2 + 3H_2O + 9N_2$) or lower, indicating that in CR_{N2O} N_2O completely reacted with C_3H_6. The addition of NO to the feed (CR_{sim}) had no effect on N_2O reduction.

3.1.3. Simultaneous abatement of NO_x and N_2O: dependence of activity on C_3H_6 and O_2 amount in the feed

The comparison between catalytic results in the presence and in the absence of O_2 indicated on both catalysts a selectivity problem: notwithstanding in the absence of O_2 C_3H_6 reacted with NO and N_2O, in the presence of O_2 it preferentially burned. Because O_2 is a co-existent reagent in real exhaust gases, to find the gas-mixture
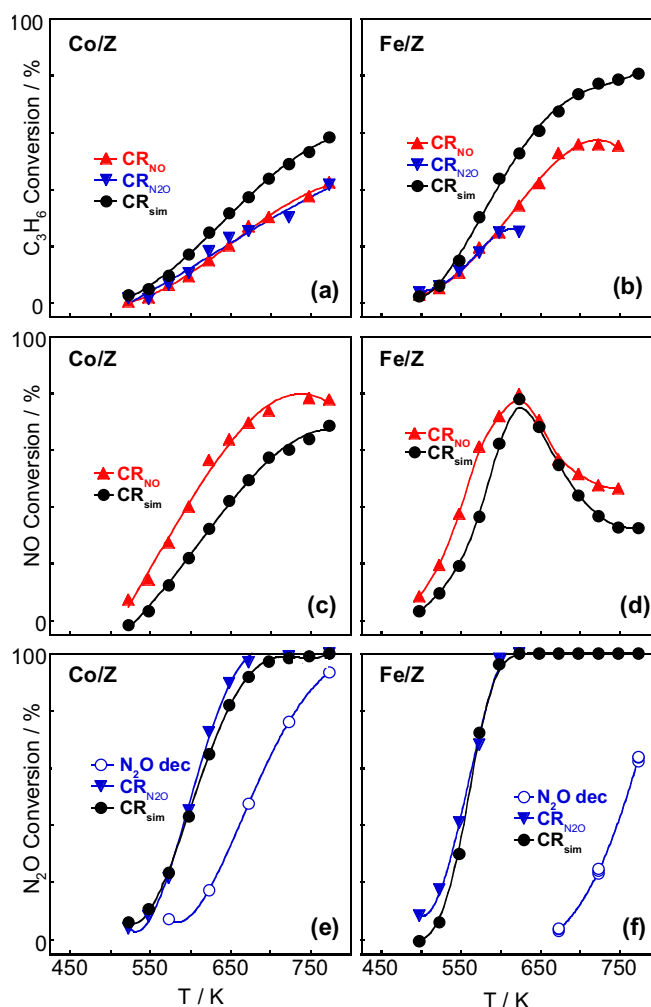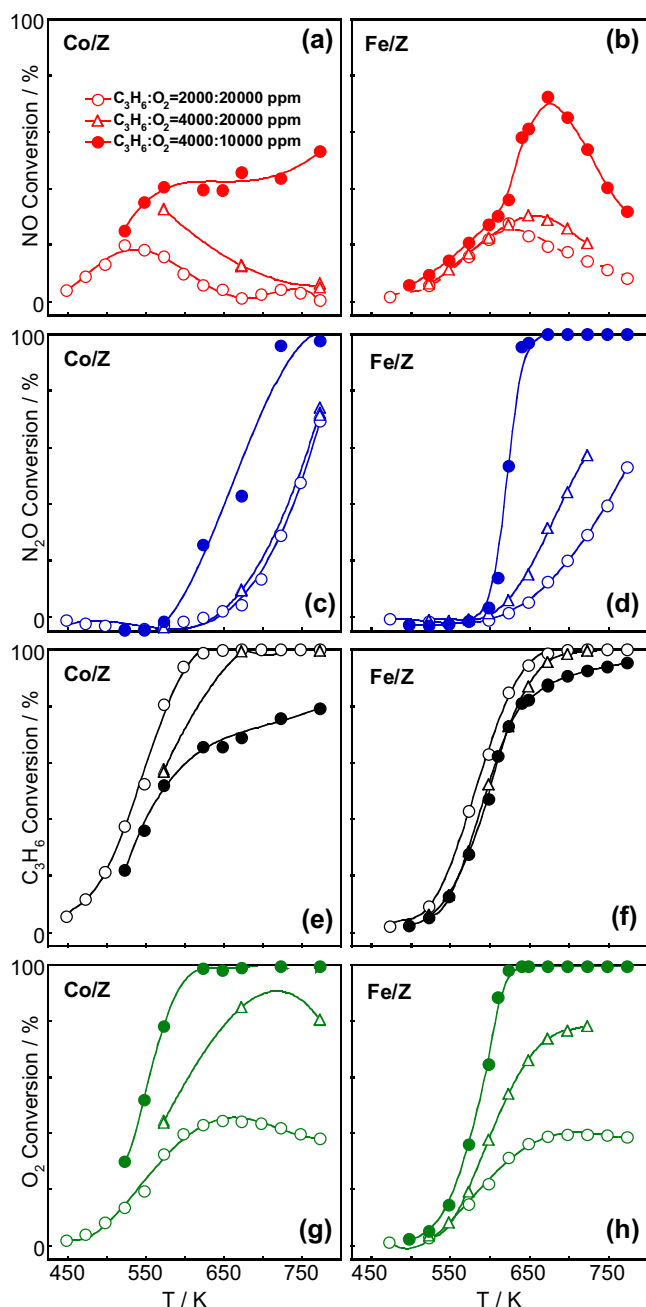

Fig. 5. Comparison between CR_{sim} and related reactions (CR_{NO}, CR_{N2O} and N_2O decomposition) on Co/Z (Section a, c, e) and Fe/Z (Section b, d, f). Percent C_3H_6, NO and N_2O conversion as a function of temperature.
Reactant mixtures: N_2O (4000 or 0 ppm), NO (4000 or 0 ppm), C_3H_6 (2000 or 0 ppm). Reactions as indicated.

composition yielding an efficient NO and N_2O simultaneous abatement, we modified the C_3H_6 and O_2 relative amount in the feed

By doubling C_3H_6 content from 2000 to 4000 ppm (Fig. 6) on both Fe/Z and Co/Z in SCR_{sim} (i) the maximum value of NO conversion in the volcano-shaped curve increased, (ii) N_2O conversion increased on Fe/Z and remained unchanged on Co/Z, (iii) C_3H_6 conversion was 100% above 673 K, and (iv) O_2 conversion increased, remaining below 100%.

By subsequently halving O_2 content from 20000 to 10000 ppm (Fig. 6) on both catalysts NO and N_2O conversion markedly increased. With this mixture, above 600 K O_2 was completely consumed and C_3H_6 was not, driving the reaction conditions near to that of CR_{sim}. In fact, residual C_3H_6, still available above 600 K, reduced N_2O and NO, as in CR_{sim}: (i) N_2O conversion reached 100% on both catalysts, and (ii) NO conversion increased, monotonically on Co/Z, and volcano-shaped on Fe/Z (compare Fig. 6 with Fig. 4). Unlike CR_{sim}, by using this feeding mixture, with C_3H_6 4000 ppm and O_2 10000 ppm, no by-products were formed and the two systems efficiently abated NO and N_2O (CO_2 selectivity 100%), Co/Z in the range 723–773 K and Fe/Z in the range 648–698 K.
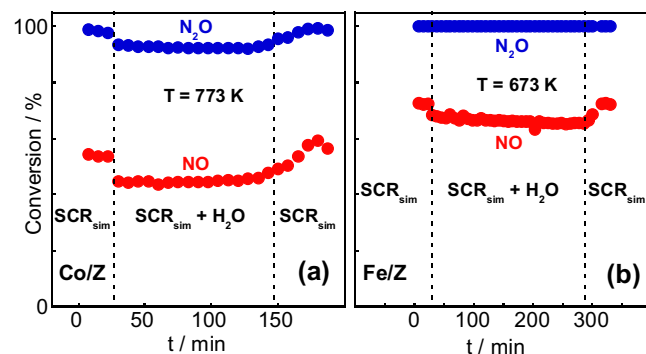
Fig. 7. SCR$_{sim}$ reaction on Co/Z (Section a) and Fe/Z (Section b), in the presence or in the absence of H$_2$O vapour in the reactant mixture: percent NO and N$_2$O conversion as a function of time on stream.

Reactant mixtures: in SCR$_{sim}$, NO:N$_2$O:C$_3$H$_6$:O$_2$ = 4000:4000:4000:10000 ppm (v/v); in (SCR$_{sim}$ + H$_2$O), NO:N$_2$O:C$_3$H$_6$:O$_2$:H$_2$O = 4000:4000:4000:10000:10000 ppm (v/v).

On the whole, on both catalysts the reversibility of the deactivation by H$_2$O suggested that it was due to reversible H$_2$O adsorption/desorption phenomena. On the contrary, analogous treatment on tmi-zeolites failed to restore the activity [24], because zeolite exposure to H$_2$O at the reaction temperature may cause irreversible de-alumination or tmi-metal oxide segregation.

3.2. Stability of Me^{n+} species after catalytic experiments: XRD, UV–vis DRS, and FTIR characterization

To verify the stability of Me^{n+} active species, we characterized Co/Z and Fe/Z at the end of catalytic experiments (aged samples) by XRD, Uv–vis DRS and FTIR. We compared the results on aged samples with those on calcined samples, that we extensively reported in previous papers [20,21] and now briefly summarise.
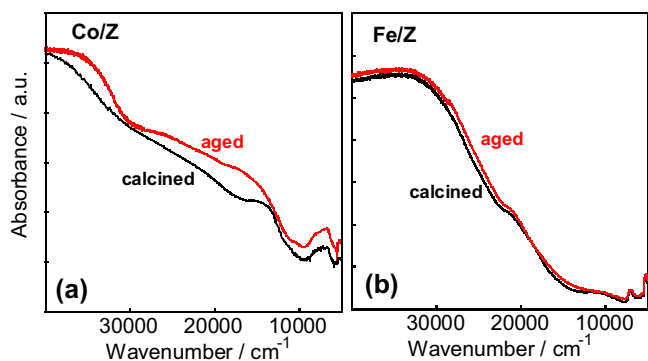
On calcined CoO$_x$/ZrO$_2$ [20] and FeO$_x$/ZrO$_2$ [21] with different Me-content (Co up to 5.1 and Fe up to 5.8 atoms nm^{-2}) FTIR characterization by CO and NO adsorption showed that tmi species were highly dispersed, up to 2.0 atoms nm^{-2} for cobalt and up to 2.8 atoms nm^{-2} for iron. Previous characterization of calcined Co/Z and Fe/Z with 2.2 atoms nm^{-2} (XRD, UV–vis DRS and FTIR by NO adsorption) indicated that they contained mainly dispersed Me^{n+} species. XPS characterization showed that Fe^{3+} (with low amount of Fe^{2+}), and Co^{2+} (with low amount of Co^{3+}) oxidation states were stabilized on ZrO$_2$ [20–22].

XRD spectra of aged samples were similar to those of calcined samples, showing reflections of monoclinic ZrO$_2$ alone: segregated particles of cobalt or iron oxides, if present, were smaller than 5 nm (data not shown).

The UV–vis DRS spectrum of Co/Z aged sample (Fig. 8a) showed bands at 7500 and 14000–22000 cm^{-1}, consistent with both octahedral Co^{2+} [25] and low amount of Co$_3$O$_4$ [20], and, despite a higher intensity of octahedral Co^{2+} bands, had a profile similar to that of calcined sample.

The UV–vis DRS spectra of the calcined and aged Fe/Z samples (Fig. 8b) were almost identical, consisting of very weak bands at about 21000, 18800 and 12000 cm^{-1}, typical of Fe^{3+} complexes [21,26].

The FTIR spectra after NO adsorption on aged Me/Z samples showed bands of Me^{n+}-nitrosyls (Me^{n+} = Co^{2+} or Fe^{2+}) [20,21] in the same position and with similar width of those obtained on the corresponding calcined samples (Fig. 9a and b). This result indicated that the exposed Me^{n+} species on aged catalysts had Lewis acid strength and heterogeneity similar to those in calcined samples. Moreover, the overall intensity of the Me^{n+}-nitrosyl bands on aged catalysts was similar to that on the corresponding calcined

Fig. 6. SCR$_{sim}$ reaction on Co/Z (Section a, c, e, g) and Fe/Z (Section b, d, f, h), using C$_3$H$_6$ + NO + N$_2$O + O$_2$ gas mixtures with different C$_3$H$_6$ and O$_2$ amount in the feed, C$_3$H$_6$:O$_2$ ratio as indicated. Percent NO, N$_2$O, C$_3$H$_6$, and O$_2$ conversion as a function of temperature.

3.1.4. Simultaneous abatement of NO$_x$ and N$_2$O: activity in the presence of water vapour

In the mixture condition in which both catalysts efficiently abated NO and N$_2$O (NO:N$_2$O:C$_3$H$_6$:O$_2$ = 4000:4000:4000:10000 ppm) we investigated the stability of catalyst activity after water addition (10000 ppm) to the feed. On both catalysts, at the temperature at which each system yielded the maximum NO and N$_2$O conversion in dry feed, after H$_2$O addition the activity little decreased or did not, remaining stable as a function of time on stream. The activity was reversibly restored when H$_2$O was eliminated from the feed (Fig. 7).

Fig. 8. In situ UV–vis DRS spectra of Co/Z (Section a) and Fe/Z (Section b), after calcining at 823 K for 5 h (calcined samples) and at the end of all catalytic experiments (aged samples).
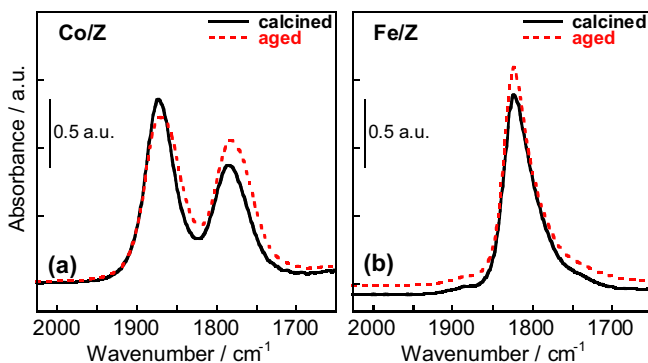
Fig. 9. FTIR spectra of NO adsorbed (at equilibrium pressure 50 Torr) on Co/Z (Section a) and Fe/Z (Section b), after calcining at 823 K for 5 h (calcined samples) and at the end of all catalytic experiments (aged samples).

samples (Fig. 9a and b), indicating after catalytic experiments no change in the amount of dispersed Me^{n+} species.

On the whole characterization of aged samples suggested that both Co/Z and Fe/Z catalysts contained mainly dispersed Me^{n+} species and that, although a rearrangement of surface tmi species during catalysis cannot be excluded, on both catalysts no significant segregation phenomena occurred in hydrothermal conditions.

4. Conclusions

CoO_x/ZrO_2 and FeO_x/ZrO_2 catalysts, containing mainly dispersed tmi species, in the presence of O_2 excess are scarcely active and unselective for the separate NO and N_2O abatements with C_3H_6 and are ineffective for their simultaneous abatement. Because C_3H_6 preferentially yielded combustion to CO_2, NO is poorly reduced and N_2O is abated via both reduction and decomposition. When the simultaneous abatement is carried out in the absence of O_2, C_3H_6 reduces NO and N_2O. The two systems operate in different temperature ranges with competitive formation of by-products.

The activity for the simultaneous NO and N_2O abatement with C_3H_6 in the presence of O_2 strongly depends on the C_3H_6/O_2 feed-ing ratio. When the C_3H_6 amount is increased and that of O_2 is decreased (C_3H_6 from 2000 to 4000 ppm and O_2 from 20000 to 10000 ppm), O_2 is completely consumed and the residual C_3H_6 efficiently reduces NO and N_2O in the same temperature range and with negligible formation of by-products.

In hydrothermal conditions, CoO_x/ZrO_2 and FeO_x/ZrO_2 are slightly and reversibly deactivated, with catalytic activity stable as a function of time on stream. Characterization by XRD, UV–vis DRS, and FTIR, after catalytic experiments, showed that dispersed Co^{2+} and Fe^{3+} species are stable on zirconia surface and that no significant segregation phenomena occurs in hydrothermal conditions.

From an applied viewpoint, CoO_x/ZrO_2 and FeO_x/ZrO_2 catalysts, modulating the C_3H_6/O_2 feeding ratio, are possible candidates to carry out in different temperature ranges the simultaneous abatement of NO and N_2O with propene.

Acknowledgements

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